S&C FY02 ANNUAL REVIEW MEETING

Solid State Sensors for Monitoring Hydrogen in IOF Process Streams

Anthony McDaniel, D. Morrison (SNL)

M. Horn, R. Jayaraman, R. Messier, R. McGrath (PSU)

F. Schweighardt (APCI)

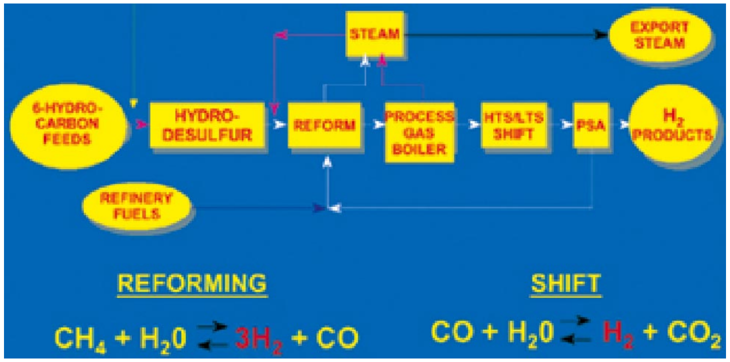
S. Huenemeier (DCHT)

Develop sensor technology for “in-process” monitoring of hydrogen

- **Measuring H_2 content of process streams critical to IOFs:**
  - **Glass**
    - surface defects in tin float baths
  - **Chemicals**
    - ammonia and polyolefin manufacture, batch hydrogenation
  - **Petroleum**
    - hydrogen recovery / cogeneration for oil refining
- **Non-IOF applications**
  - **H_2 generation, storage, utilization (fuel cells)**
- **Aggressive environments**
  - **Contain reactive gases and/or liquids**
  - **Elevated temperatures and/or pressures**

Research and development focused on hydrogen cogeneration

- **Air Products and Chemicals, Inc. HyCO process**
  - **Reforming of refinery off-gas (hydrocarbons)**
  - **Produce 1.3 billion SCF per day H_2 in the U.S.**
- **Quantify H_2 content in refinery off-gas feedstock & in-process streams**
  - **Maximize plant performance**
    - bypass H_2-rich feed streams
    - minimize gas venting
  - **Reduce power consumption**
    - optimize steam-to-carbon ratio in reformer and shift reactors



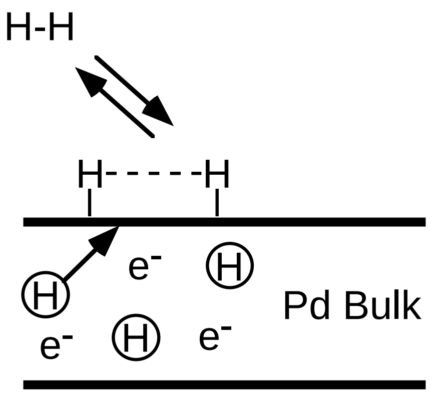
- **Overall goal**
  - **On-line hydrogen analysis (0.5-100% H_2, <5 sec)**

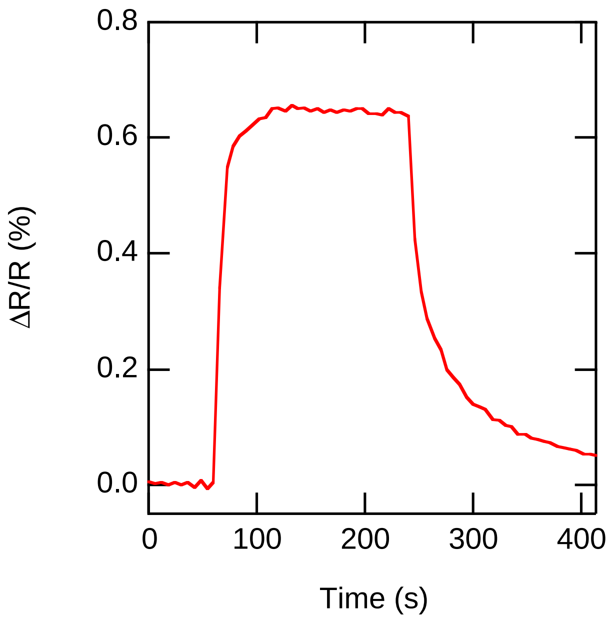
S&C FY02

Background on H_2 chemical-resistor technology

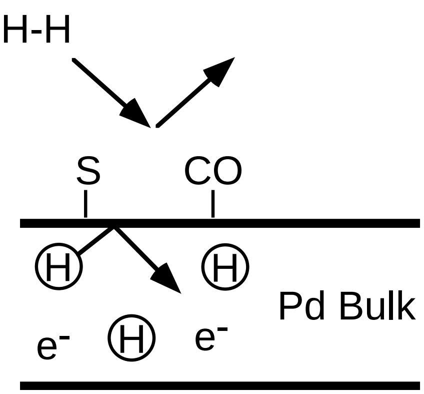
- **Thin ohmic film of transition metal alloy (Pd, Ni)**
- **Principle of operation**
  - **Surface chemistry moderates response**
    - dissociative adsorption of H_2
  - **Protons diffuse into bulk altering I-V characteristics**
    - increase electrical resistance
  - **Adsorption isotherm obeys Sievert's Law**

$$\ln\sqrt{P_{H_2}} = \ln\left(K \cdot \frac{n}{1-n}\right); \quad n = \frac{\mathrm{H}}{\mathrm{Pd}}; \quad K = \exp\left[-\frac{\Delta H^o}{2RT} + \frac{\Delta S^o}{2R}\right]$$





Technical risks/innovation



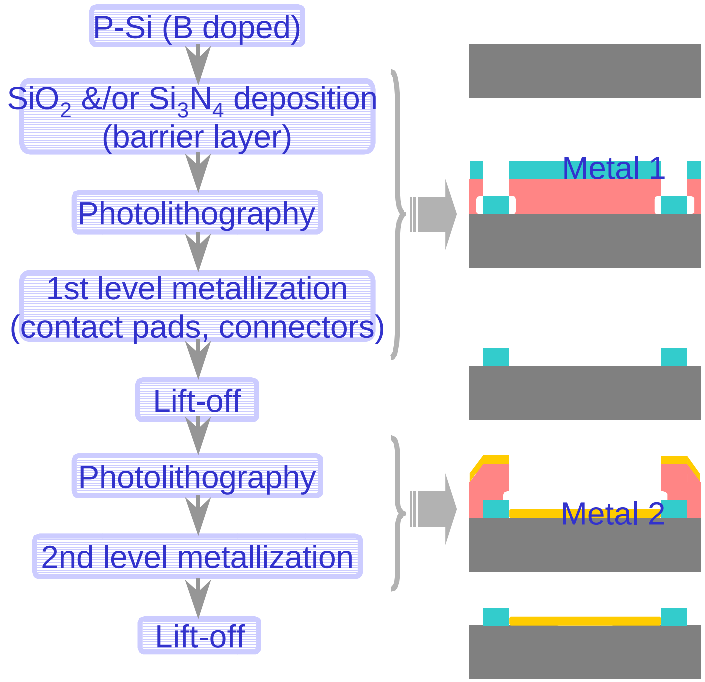
- **Technical risks associated with industrial application**
  - **Poisoning of catalytic surface by CO and sulfur (H_2S, RR'S, RHS)**
  - **α-β phase transition at large H_2 pressure**
- **Innovation**
  - **Application of selectively permeable membranes**
  - **Optimization of alloy composition**
- **At present GC and GC/MS used to measure H_2 in process streams**
  - **Large, complex, costly analytical instruments**
- **H_2-chemresistor is simple, inexpensive, and amenable to distributed sensing applications**

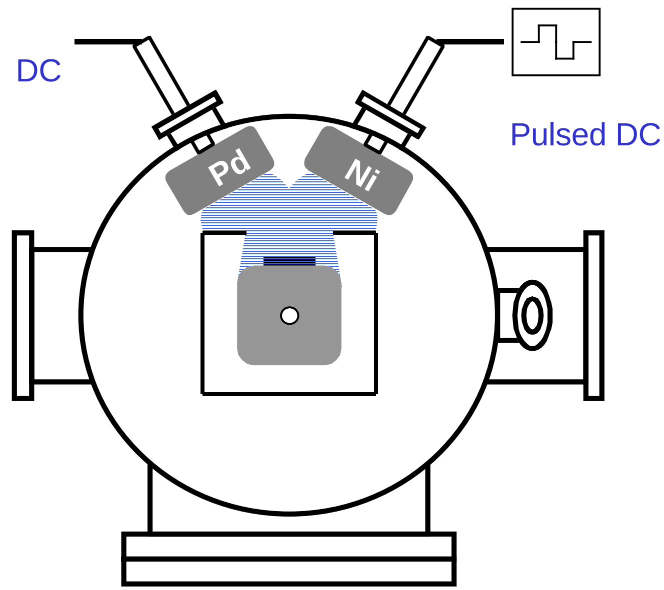
Task performance

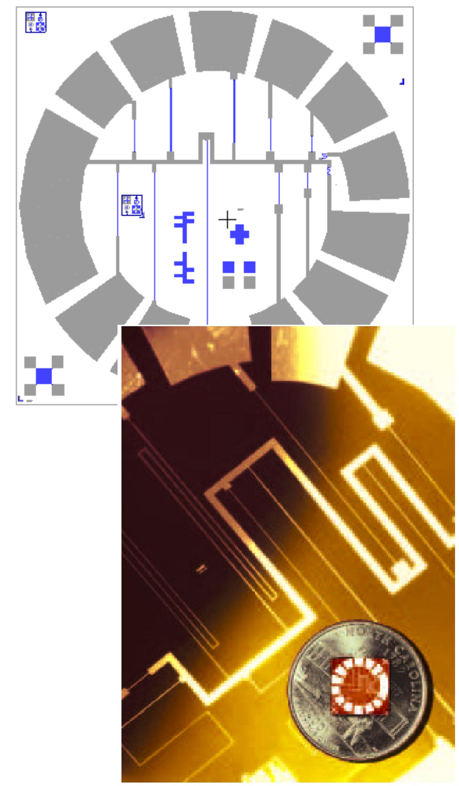
Past Technical Milestones

Milestone		Due Date	Completion Date	Comments
PSU	Fabricate H_2-chemresistor test structures; vary alloy composition, incorporate membranes	10/01 3/02-1/03	9/01	ongoing work
SNL	Construct laboratory testing facility	11/00 1/02	1/01 4/02	flow cell high-pressure cell
SNL	Develop surface chemistry models for predicting sensor performance	10/01	10/01	further modeling efforts abandoned
SNL	Characterize sensors, determine failure modes, evaluate design changes	1/03		ongoing work
DCHT	Provide equipment for field tests	7/00 7/02	7/00	
APCI	Upgrade and prepare field unit for pilot plant testing	2/02		in progress
APCI	Pilot plant testing	5/02 7/02		in progress

Fabrication of H_2-chemresistor test structures

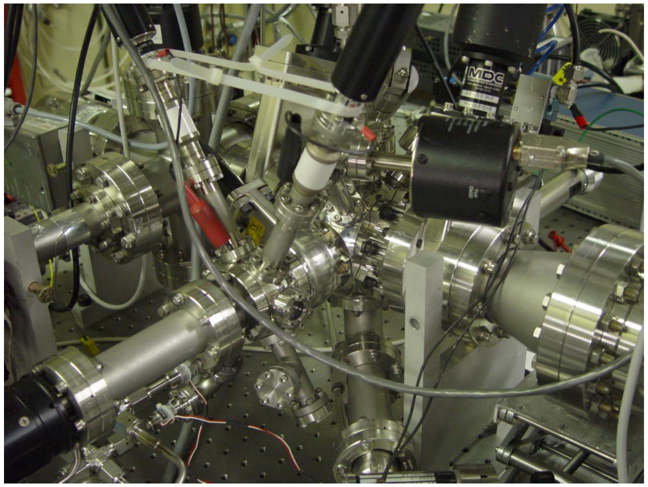




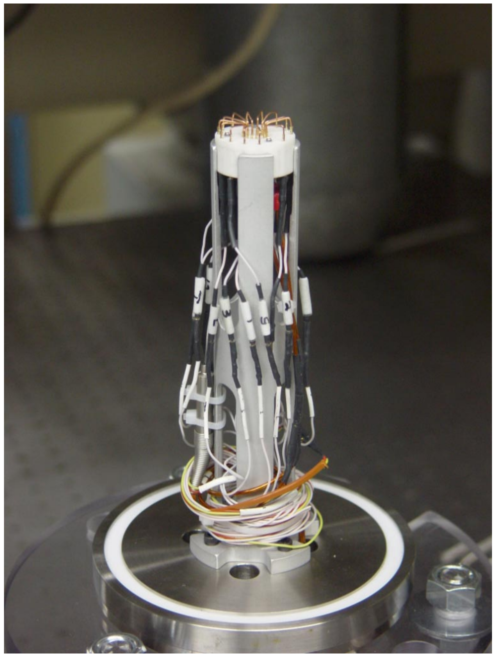


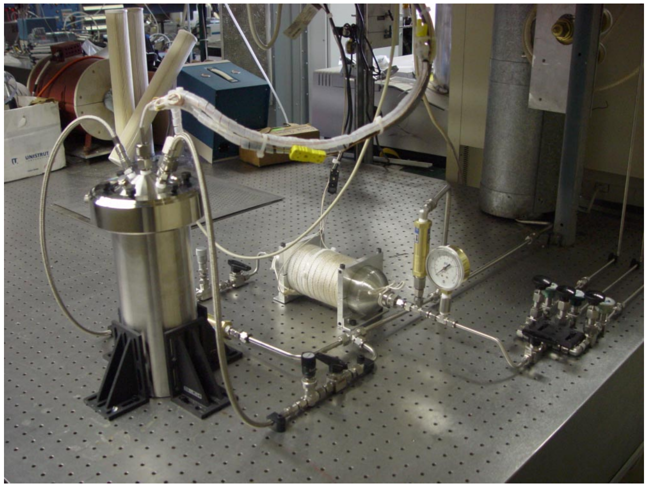
- **Multi-mask, contact lithography and lift-off**
- **DC and pulsed DC magnetron sputtering of metals**
  - **Precise control of composition, morphology, and stress**

Laboratory testing facilities



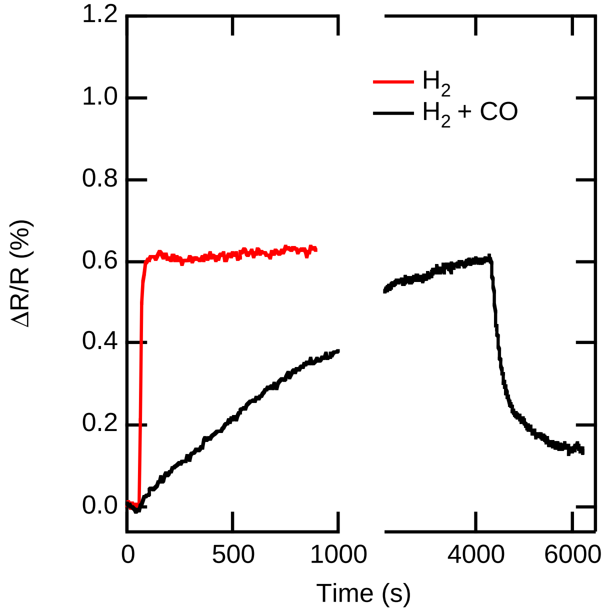
- **Flow cell**
  flexible gas manifold
  integrated MS
  low pressure
  dynamic studies

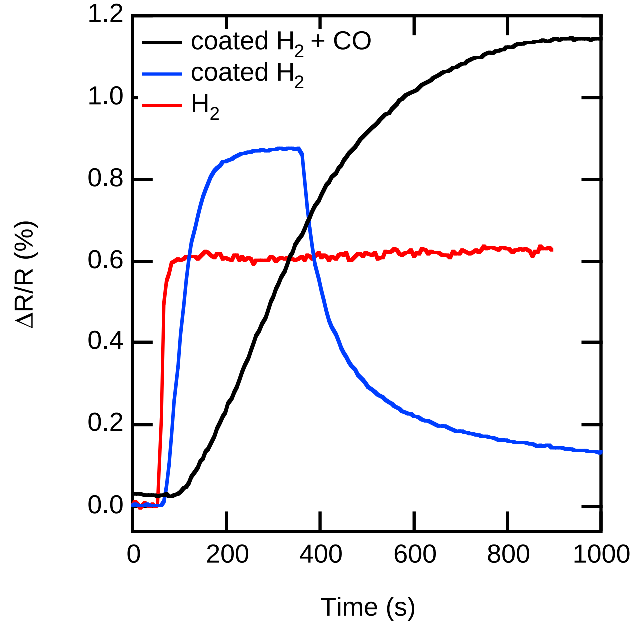


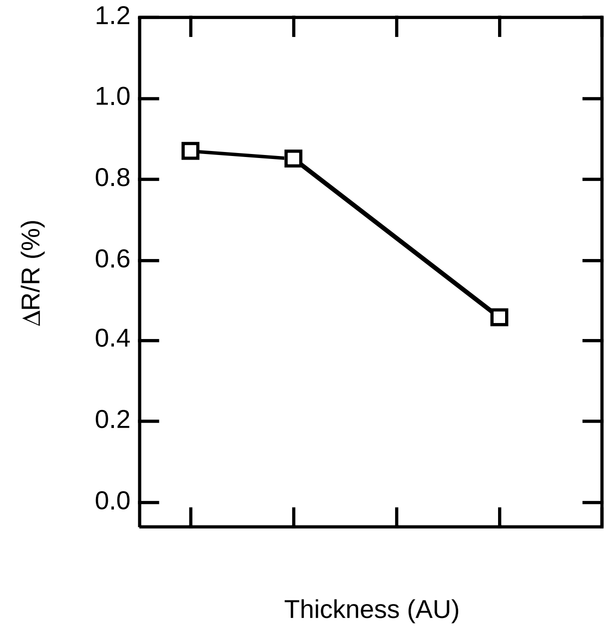


- **High-pressure cell**
  "Parr Bomb"
  0-2000 psia

Effects of CO and permeable membranes

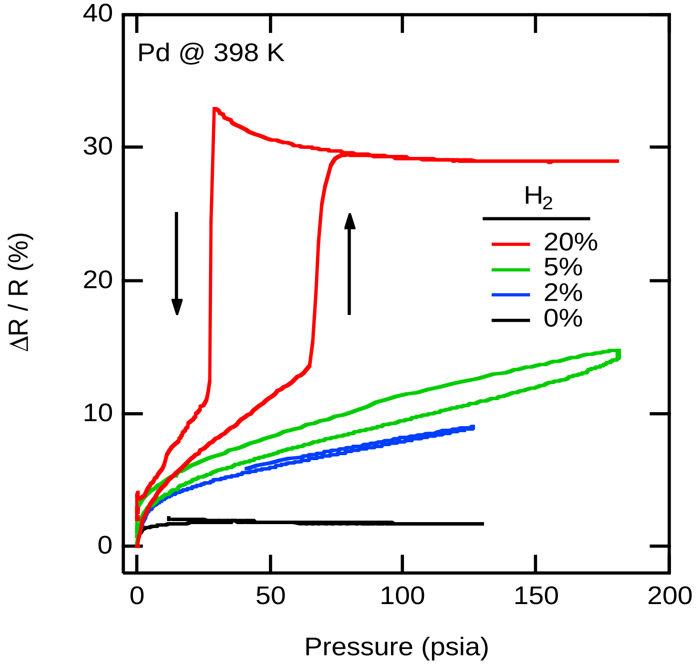


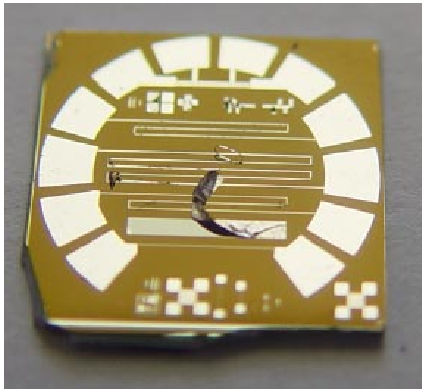


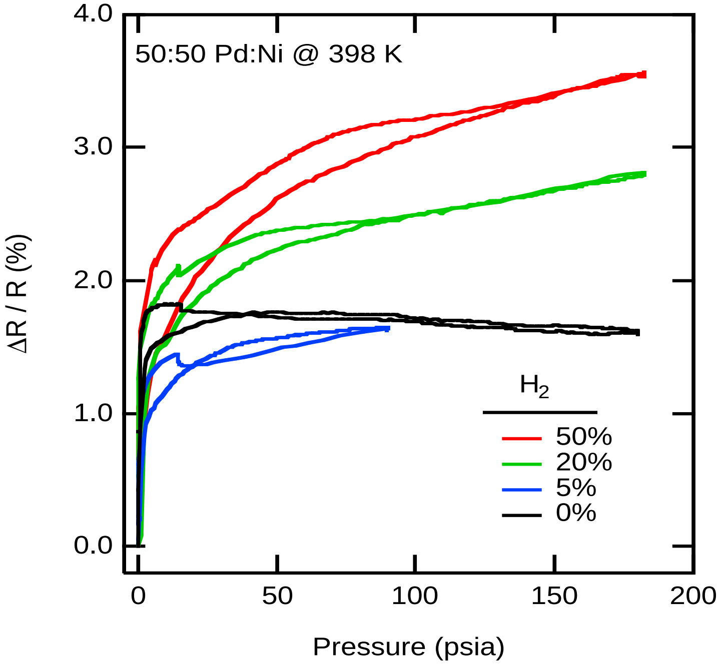


- **Surface chemistry modified by co-adsorbates**
  - **CO slows sensor response to H_2, but does not attenuate signal**
- **Application of permeable membrane mitigates effect of CO**
  - **Need to optimize coating material and film thickness**

High pressure failure mode and effects of alloy







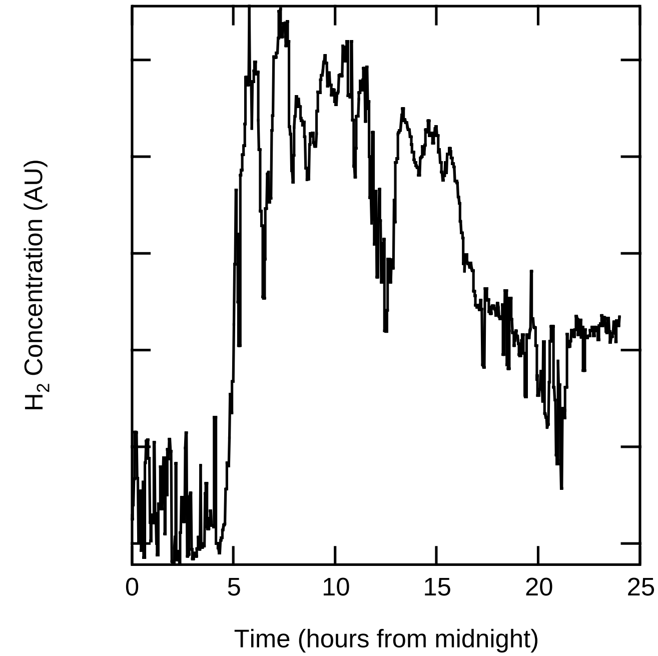
- **13 psia H_2 induces α-β phase transition in Pd thin film**
  - **Sensor does not respond predictably in two-phase region**
  - **Lattice expansion delaminates film**
- **Pd/Ni alloy extends operation to higher H_2 partial pressures**

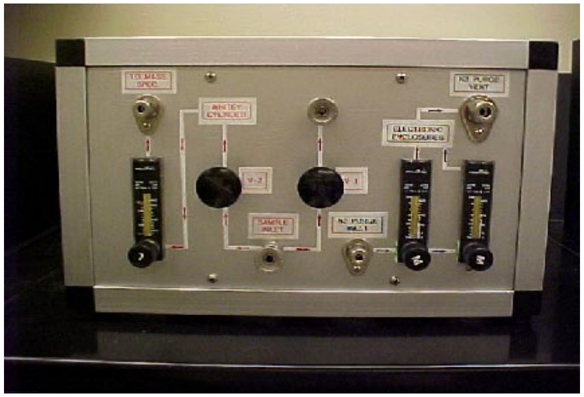
AIR PRODUCTS DCH TECHNOLOGY PENNSTATE

S&C FY02

Field testing

- **Air Products & Chemicals**
  - **HyCO plant Wilmington, CA**
  - **H_2 content of refinery feed gas**
  - **On-line sampling, DCH chip**





S&C FY02

Commercialization

- **Proposed future plant tests**
  - **On-line sampling with current field unit**
    - DCH chips, upgraded electronics
    - real-time pressure compensation
  - **Tennessee Eastman-Chemicals**
    - chemical batch hydrogenation
  - **Air Products & Chemicals**
    - HyCO and ammonia plant
  - **Exxon-Mobil (Tentative)**
  - **Dow (Tentative)**
- **Commercialization partner DCH Technologies**
  - **Identified market opportunities and remain interested in technology**

Performance merits for H_2 cogeneration

- **Improving energy efficiency for hydrogen cogeneration**
  - **Measure H_2 in refinery feed and process streams**
    - Redirect H_2-rich feed gas
    - Optimize steam-to-carbon ratio
- **Redirecting H_2 rich refinery feed**
  - **Estimated improvement in efficiency is 0.4% per plant**
    - assume 6 units installed
  - **Save 1.24 BTU/SCF H_2 @ 0.5-1x10^6 SCF H_2/day/plant**
  - **Save 2.2x10^8 BTU/day in U.S. facilities**
- **Plant optimization would yield even greater energy savings!**

Performance merits for hydrogenation plant

- **Batch hydrogenation**
  - **Monitor H_2 as a function of time**
    - 1% improvement in sustained catalytic efficiency
    - Extend life of catalytic bed by 0.5 years
- **More than 400 hydrogenation facilities in U.S.**
    - Save $1.5-2.5x10^8/year @ $3.0-5.0x10^5/year/plant
    - Extending intervals between catalyst replacement could save $2.4x10^7/year
- **Mass spectrometer installed cost $3.0x10^5/unit**
- **H_2 Solid state sensor installed cost $1.5x10^4/unit**
  - **Chemresistor chips are a small fraction of the installed cost!**

Path forward

- **Next steps**
  - **Identify optimal alloy composition for various applications**
    - Refinery feed (100 psig), reformer, PSA (300 psig), purified plant H_2 (100-2000 psig)
  - **Identify optimal coating material and thickness**
    - Mitigate the effects of contaminants, cross sensitivity to other matrix gases
  - **Develop fabrication protocols for chip production on 4 and 6 inch wafers**
  - **Prototype and test advanced sensing elements**
    - coatings, alloys, on-chip pressure compensation
  - **Transfer technology to commercial partner**